

Dynamics of excited triplet state of π -conjugated poly(3-n-octylthiophene) in solution

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Dynamics of the excited triplet state of π -conjugated poly(3-n-octylthiophene) in solution was studied by nanosecond laser flash photolysis. The time-resolved absorption spectra for poly(3-n-octylthiophene) in THF showed the triplet–triplet (T–T) absorption band near 800 nm. The fast- and slow-decay components were observed in absorption time profiles of the T–T absorption band, and the ratio of the two components significantly depends on both the polymer concentration and the excitation laser power. With an increase in the excitation laser power, the density of excited triplet state on a polymer chain increases, resulting in the increase of the fast-decay component. The fast-decay component was attributed to the intra-chain T–T annihilation. The rate constant of intra-chain T–T annihilation is three orders of magnitude larger than the diffusion-controlled rate of small molecules in solution as derived from the Debye equation. On the other hand, the slow-decay component consisted of mixed-order kinetics with first- and second-order. The first-order part was ascribed to the intrinsic lifetime of the triplet state and the slow second-order part to the inter-chain T–T annihilation, which becomes pronounced when the concentration of polymer is high. The fraction of the fast-decay component in whole-decay components showed significant dependence on the number of triplet state moieties on a polymer chain. © 1998 Published by Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Consecutive excited energy transfer between chromophores along a single chain is a characteristic phenomenon of polymer systems and is known as excited energy migration. The study of excited energy migration is important in the understanding of the characteristic phenomena of polymers, such as energy transfer processes, in biosystem and photo-functional polymer materials. So far, studies have mainly been performed in side-chain type polymers with a flexible main-chain having pendant chromophores, and the energy migration processes have been explained as a hopping process from the chromophore in the excited state to the other chromophore in the ground state¹. The resonance energy transfer mechanism (Förster type mechanism) is attributed to the excited singlet energy migration process, and the exchange energy transfer mechanism (Dexter type mechanism) to the excited triplet energy transfer process. In contrast to the many studies concentrating of the side-chain type polymers, fewer studies have examined main-chain type polymers.

For the π -conjugated polymers such as poly(phenylacetylene)^{2–6}, the excited singlet energy migration was recently investigated using femtosecond and picosecond time-resolved spectroscopies^{7–13}. However, most π -conjugated polymers are usually insoluble and deep-doped, which prevents photochemical study in solution. If dynamic behavior for the isolated polymer chain is studied in a dilute solution, the one-dimensional excited energy

migration along the π -conjugated main chain, which is the characteristic behavior of polymers, can be obtained. Recent developments in the synthesis of soluble conductive polymers make it possible to investigate the photophysical properties of the π -conjugated polymer in solution. In contrast to the studies of the excited singlet energy migration for some π -conjugated polymers, few studies have been made of the excited triplet energy migration on π -conjugated polymer.

The first process of the excited triplet state, the formation of excited triplet state from excited singlet state, takes place via intersystem crossing. The transverse process of the excited triplet energy in a polymer system can be classified into two types: energy migration, which occurs between the nearest neighbor chromophores along the polymer chain; and energy transfer, which occurs between the non-nearest neighbor chromophores in a single polymer chain. In addition, inter-chain energy transfer may be possible when the concentration of the polymer is high. Finally, the excited triplet energy is dissipated by mainly intrinsic unimolecular deactivation (nonradiative transition and phosphorescence) and by triplet–triplet (T–T) annihilation. In a polymer system, the T–T annihilation process can be classified into two types: intra-chain and inter-chain T–T annihilation.

The excited triplet energy migration for some side-chain type polymers has been studied by phosphorescence spectra in rigid matrix or in film, neither of which allows to distinguish the inter-chain T–T annihilation from intra-chain process^{14,15}. The laser flash photolysis technique is superior to phosphorescence measurement for investigation of dynamics of the excited triplet state. In the 1970s, some laser flash photolysis studies were carried out for the T–T

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annihilation process of side-chain type polymers in solution^{16–18}, but at that time it was difficult to analyze the decay of T–T absorption band, including plural competitive deactivation processes. Recently, studies of T–T annihilation via excited energy migration in side-chain type polymer in film systems have been carried out using the laser flash photolysis method¹⁹. In film systems, the triplet energy transfer occurs with an electron exchange process only when the donor and the acceptor are close enough to overlap their electron clouds, depending on the distance between two chromophores in the Dexter type energy transfer¹. For these reasons, long-distance energy migration is difficult to achieve in films of side-chain type polymers.

In this paper, we report the excited triplet state dynamics of π -conjugated poly(3-*n*-octylthiophene) (P3OT) in solution as studied by laser flash photolysis. Dynamics of the excited triplet state of thiophene oligomer (as a model small molecule compound) was also studied to compare with that of the polymer. The isolated polymer chain in dilute solution enables observation of the intra-chain T–T annihilation, giving information about the one-dimensional excited triplet energy migration process in polymer chains.

EXPERIMENTAL

P3OT was prepared by the polymerization of 3-*n*-octylthiophene (Tokyo Chemical Industry Co., Ltd.) with iron (III) chloride (anhydrous) as an oxidizing agent in chloroform at 30°C for 2 h^{20,21}. The dark red polymer was de-doped using sodium hydrosulfite and purified by reprecipitation using methanol as a precipitant. The molecular weight and the polydispersity were determined to be 2.0×10^5 and 2.54×10^5 , respectively, by GPC using mono-disperse polystyrene as a standard. The regularity of the polymer structure was checked by ¹H-NMR spectra in chloroform-*d*₁ as solvent. Integration of the proton peak at the 4-position on the thiophene ring confirmed head-to-tail structure (76% of total)^{22,23}. 2,2':5',2''-terthiophene (3T) was obtained from Aldrich. P3OT and 3T was dissolved in spectroscopic grade THF, and the sample solution in a square quartz cell of 1 cm path length was deaerated by argon bubbling before measurement. The overlap concentration of poly(3-*n*-hexylthiophene) is reported to be higher than 2×10^{-2} g ml⁻¹ (120 mM in monomer unit) in THF^{24,25}. The measurements were carried out far below the overlap concentration. All measurements were made at 22 °C.

Nanosecond laser flash photolysis experiments were carried out with a Nd:YAG laser (Quanta-Ray, GCR-130, 6 ns FWHM). P3OT solution was excited at 355 nm, and the probe light from a xenon flash lamp passed through the sample cell was detected using a Si-PIN (Hamamatsu Photonics K.K. S1722-01) module for a short time scale (5 μ s full scale) and photomultiplier system at 800 nm (50 μ s full scale). The absorption–time profiles were recorded with a digitizing oscilloscope (HP 54510B, 300 MHz) and analyzed by a personal computer. The details of the experimental setup are described elsewhere²⁶.

RESULT AND DISCUSSION

The time-resolved absorption spectra obtained by 355 nm laser irradiation on 0.5 mM in monomer units of poly(3-*n*-octylthiophene) (P3OT) in THF are shown in Figure 1. All concentrations for P3OT are given as the averaged polymer unit, which is given by dividing the monomer unit concentration by polymerization degree $P_n = 406$. Thus

the averaged concentration of P3OT in polymer unit was 1.2 μ M. The absorption band with maximum near 800 nm was assigned to the T–T absorption band of P3OT²⁷. From the fact that O₂ quenches T–T absorption of P3OT, it is presumed that the lowest triplet energy of P3OT is higher than that of O₂ (22.5 kcal mol⁻¹). As described below, the decay of the transient band is dependent on the laser power when the concentration of P3OT is constant. Observing these transient spectra, the initial fast-decay and later slow-decay can be seen. The shape of the spectrum at 0.2 μ s (Figure 1a) is similar to that at 3 μ s (Figure 1b) keeping the absorption maximum near 800 nm. By time-resolved emission spectra, the shift of the fluorescence maximum to a longer wavelength with the time and the wavelength dependence of fluorescence decay were observed for P3OT in solution, which was caused by the relaxation of the excited singlet state by the energy migration²⁸. The decay of T–T absorption band of P3OT shows the same absorption maximum with the time, which indicates that the fast- and slow-decay components are not due to a redistribution process of excited triplet state during energy migration along conjugated main-chain and an intrinsic unimolecular deactivation process after the energy migration, respectively. The time-resolved absorption spectra obtained in a non-polar cyclohexane is similar to that in THF, supporting the assignment to the T–T absorption, but not the other transient species such as the radical cation. The rate constant for intersystem crossing k_{ISC} and quantum yield of excited triplet state formation Φ_T were determined as 1.54×10^9 s⁻¹ and 0.958×10^9 s⁻¹, respectively in our previous study²⁷. The high Φ_T value of P3OT is due to the intra-annular heavy-atom effect of the sulfur atom.

As shown in Figure 2, both the polymer concentration and the excitation laser power strongly influence the time profiles of the T–T absorption band of P3OT. At the same concentrations, as the excitation laser power increases, the density of the excited triplet state moiety in a chain increases. This is more marked in low concentration solutions (0.1 mM monomer unit = 0.25 μ M in polymer unit), the fast component decaying within about 1 μ s after the increased excitation laser pulse. At high polymer concentrations (2 mM monomer unit = 50 μ M in polymer unit), such a fast-decaying component was not observed

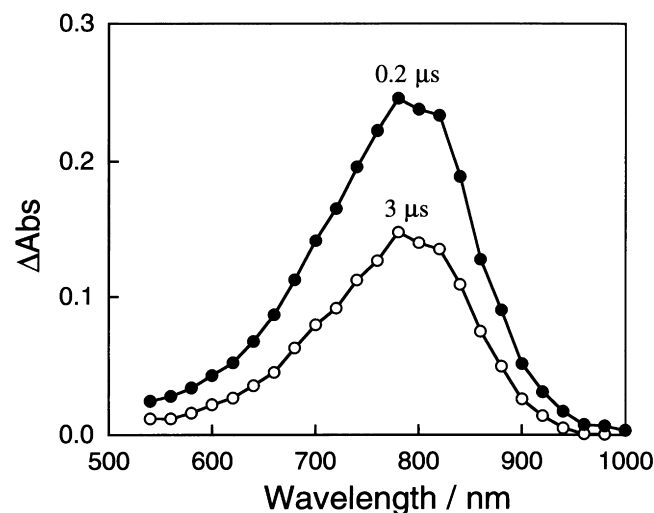


Figure 1 Time resolved absorption spectra observed by laser pulse excitation (355 nm) of P3OT (0.5 mM in monomer unit = 1.2 μ M in polymer unit) in THF, (a) at 0.2 μ s and (b) at 3 μ s. Laser power = 36 mJ

even by excitation with the high laser power. The increase of the fast-decay component with the excitation laser power at the same concentration indicates this component is an intra-chain process.

In order to examine the total decay for high P3OT concentration (50 μM in polymer unit), which is impossible using a PIN-photodiode, the decay curves were observed using a photomultiplier in the long time scale and changing the laser power. The first-order (log) and second-order (reciprocal) plots are shown in Figure 3. The initial yield of the triplet state of P3OT seems to be significantly lower than that observed with the PIN-photodiode, since the absolute yield depends on the position where passing light is monitored, which is perpendicular to the excitation laser

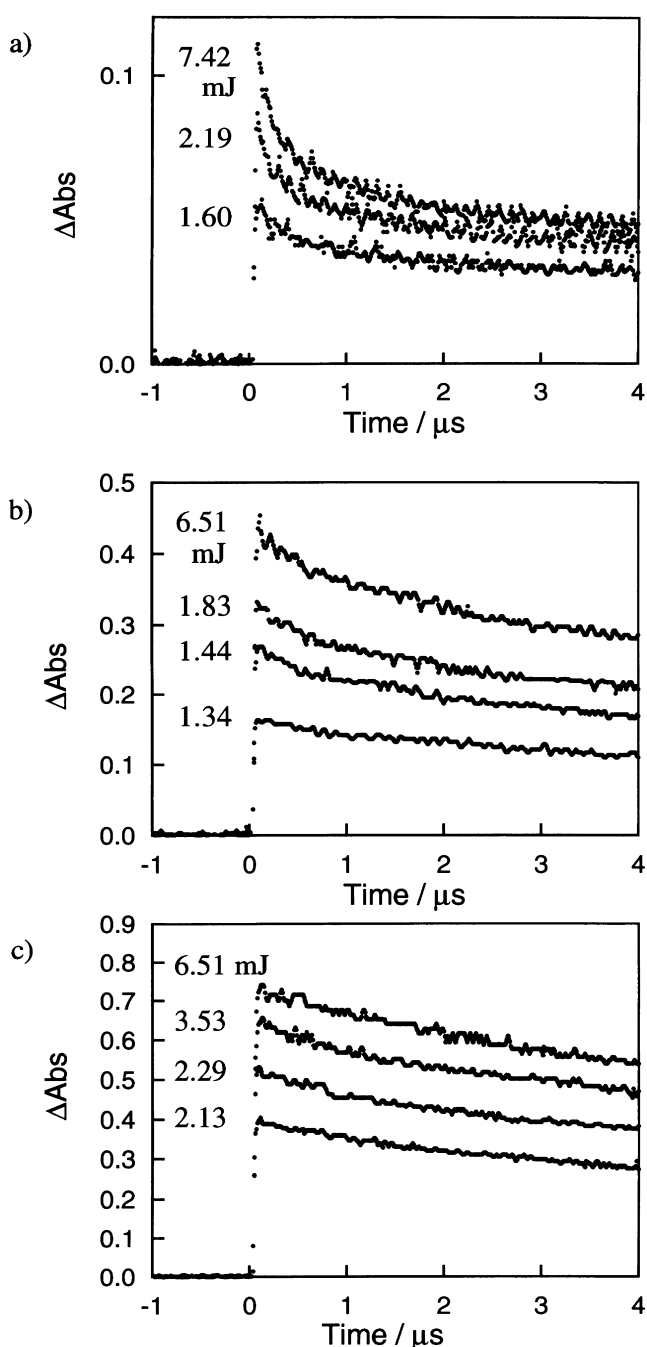


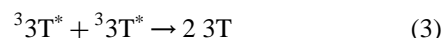
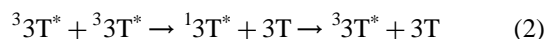
Figure 2 Absorption time profiles at 800 nm of different concentrations of P3OT in THF obtained by 355 nm excitation with different laser power: (a) 0.1 mM; (b) 1.0 mM; and (c) 2.0 mM in monomer unit. (a) 0.25; (b) 2.5; and (c) 5.0 μM in polymer unit

light. The relative absorbance is reliable for the following kinetic analysis. Because of the low sensitivities of the photomultiplier at around 800 nm, the considerable scattering of the data points were seen. Two first-order plots show a linear relation later than 5 μs , indicating that the triplet state of P3OT decays obeying first-order kinetics where the absorbance is less than $\ln(\Delta\text{Abs}) = -1.2$ ($\Delta\text{Abs} = 0.3$). From both slopes, the first-order decay rate constant (k_{1st}) was estimated to be $k_{1st} \approx 6 \times 10^4 \text{ s}^{-1}$. However, the reciprocal plots show the linear part in the initial stage of the decay (0–12 μs at 60.6 mJ laser power and 0–10 μs at 16.0 mJ laser power), which indicates the existence of the second-order decay component.

At low polymer concentration (0.25 μM in polymer unit) corresponding to the case in which both fast- and slow-decay components were observed (Figure 2a) the decay curve was observed in the long time scale (Figure 4). Since the decay curve was observed at low polymer concentration and lower laser power in order to avoid the inter-chain phenomena, the decay data with low absorbance was averaged after accumulation. In the first-order plot, the slow first-order decay was observed after the initial fast-decay in the region of 0–5 μs . By analysis of the first-order decay curve after 10 μs , in order to avoid the intra-chain phenomena, $k_{1st} = 5.11 \times 10^4 \text{ s}^{-1}$ was obtained (lifetime of ${}^3\text{P3OT}^*$ $\tau_T = 1/k_{1st} = 19.6 \mu\text{s}$).

Dynamics of the excited triplet state of thiophene trimer (2,2':5',2''-terthiophene) (3T) was studied, in order to compare with the polymer system. As shown in an inset of Figure 5, the transient absorption spectra were observed by 355 nm laser excitation of 3T (0.5 mM in oligomer unit) in THF. The absorption band with λ_{max} at 480 nm is assigned to the T–T absorption band^{29,30}. The absorption time profiles at 480 nm are shown in Figure 5. Each decay curve clearly consists of first- and second- mixed order kinetics. The decay curve analysis was carried out with consideration for the competitive reactions of unimolecular deactivation and the bimolecular process.

The deactivation processes of the excited triplet state of 3T (${}^3\text{T}^*$) can be represented by the following scheme, when concentration of ${}^3\text{T}^*$ is high:



Equation (1) is unimolecular deactivation corresponding to the intrinsic lifetime of ${}^3\text{T}^*$. Equation (2) and (3) are T–T annihilation between two ${}^3\text{T}^*$ s. If the repopulation process in equation (2) can be neglected, the mixed-order decay kinetics is analyzed by equation (4)

$$-\frac{d[{}^3\text{T}^*]}{dt} = k_{1st}[{}^3\text{T}^*] + 2k_{2nd}[{}^3\text{T}^*]^2 \quad (4)$$

where $[{}^3\text{T}^*]$ is the concentration of ${}^3\text{T}^*$, k_{1st} and k_{2nd} are the kinetic rate constants of the unimolecular deactivation process in equation (1) and the T–T annihilation process in equation (3), respectively. The k_{1st} value of ${}^3\text{T}^*$ was determined as $k_{1st} = 1.7 \times 10^4 \text{ s}^{-1}$ from the decay curve obtained by low laser power excitation to avoid the effect of T–T annihilation. The lifetime of ${}^3\text{T}^*$ is obtained as $\tau_T = 1/k_{1st} = 59.9 \mu\text{s}$, which corresponds to the reported lifetime of 57 μs in ethanol³⁰ and 62 μs in acetonitrile³¹. Then, a k_{2nd}

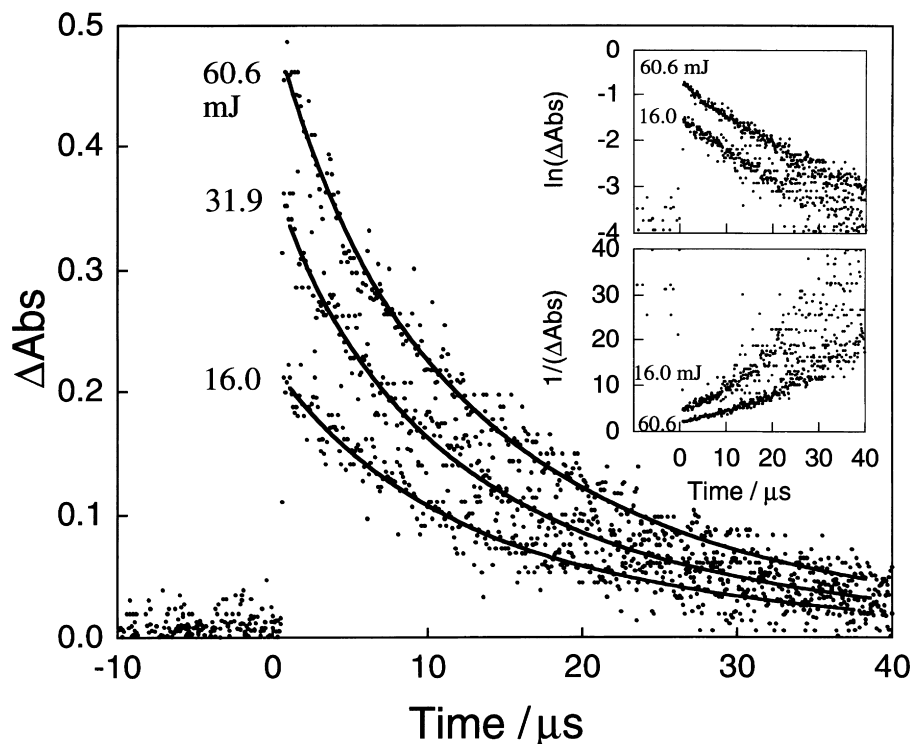


Figure 3 Absorption time profiles at 800 nm for 2.0 mM (5.0 μ M in polymer unit) of P3OT in THF obtained at various laser powers at 355 nm and the fitting curves by assuming equation (5). Inset: logarithmic and reciprocal plots of time profiles

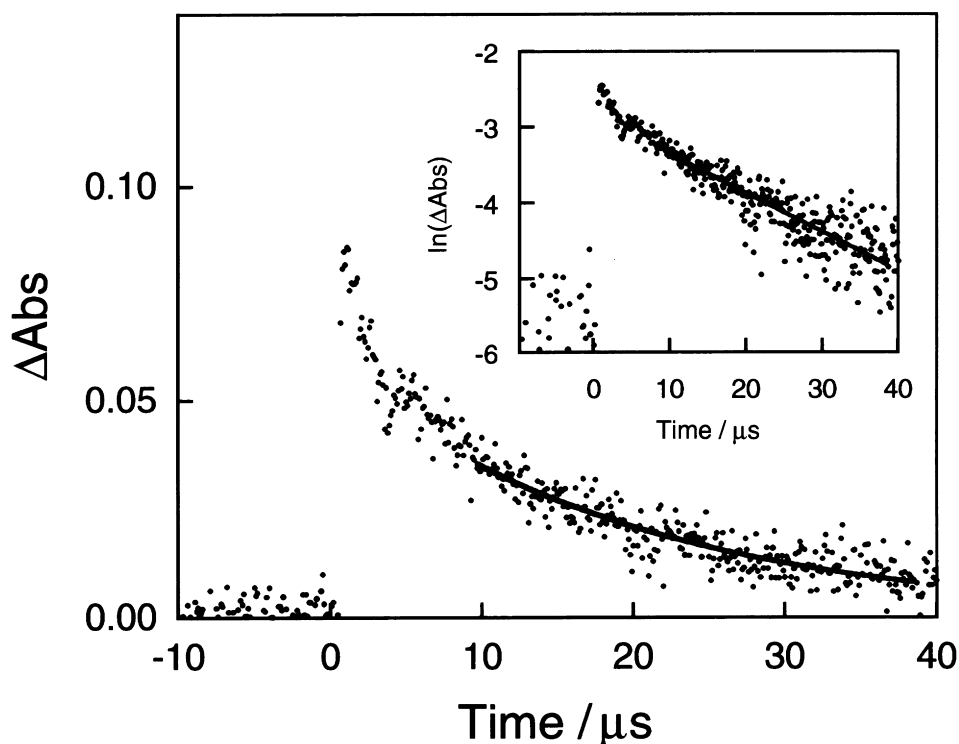


Figure 4 Absorption time profile at 800 nm for 0.25 μ M in polymer unit of P3OT in THF obtained by 355 nm laser pulse excitation. Laser power = 29.7 mJ

value was evaluated from equation (5) on fixing k_{1st} value.

$$\Delta\text{Abs} = \varepsilon_T [{}^33T^*] = \frac{1}{\left(\frac{1}{\text{Abs}_0} + \frac{2k_{2nd}}{\varepsilon_T k_{1st}}\right) \exp(k_{1st}t) - \frac{2k_{2nd}}{\varepsilon_T k_{1st}}} \quad (5)$$

where t is time, Abs_0 is the initial absorbance (at $t = 0$) and ε_T is the molar absorption coefficient of T-T absorption of 3T. The $2k_{2nd}/\varepsilon_T$ value was evaluated to be $1.6 \times 10^5 \text{ cm s}^{-1}$. On substituting $\varepsilon_T = 8.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ for ${}^33T^*$, k_{2nd} is calculated as $6.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, which is smaller than the diffusion-controlled rate constant $k_{diff} = 1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ in THF from the Debye equation³². The k_{2nd} value can be

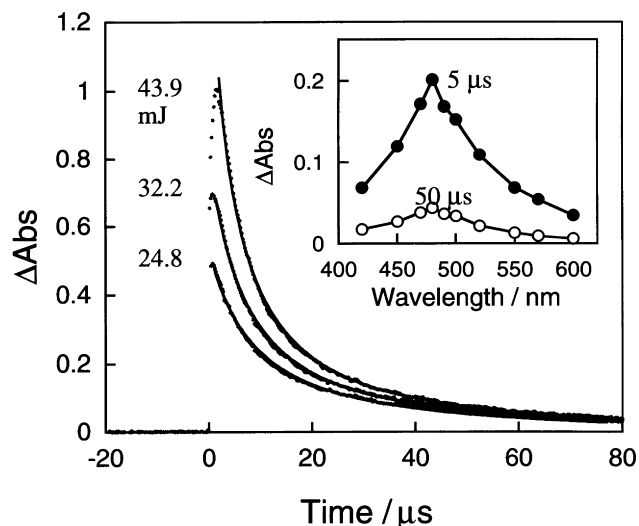


Figure 5 Absorption time profiles at 480 nm obtained by 355 nm excitation of 3T (500 μ M in oligomer unit) in THF with various laser powers. From upper 13.9, 32.2, and 24.8 mJ. Inset: transient absorption spectra of ${}^3\text{T}^*$ (17 mJ)

attributed to the rate constant for the T–T annihilation of ${}^3\text{T}^*$. The relative contribution of the T–T annihilation to the total decay can not be evaluated from equation (5). It is presumed, however, that the high concentration of [${}^3\text{T}^*$] makes a significant contribution to the T–T annihilation.

The fast-decay component within 1 μ s, which was observed for P3OT in Figure 2a was not seen for 3T by changing the concentration and laser power at a short time scale. This indicates that the fast decay observed for P3OT is characteristic to long chain polymers, and confirms the assumption of the fast-decay component being an intra-chain process. Before discussing the fast-decay component, which is superimposed on the slow-decay component, we tried to analyze the slow-decay component by the absorption time profile of high polymer concentration (5 μ M in polymer unit), in which the fast-decay component is not observed.

For the analysis of the slow-decay component observed in the long time scale, the first-order rate constants evaluated after assuming that the first-order kinetics tend to increase slightly with the concentration of the polymer; i.e., $k_{1st} = 5.11 \times 10^4 \text{ s}^{-1}$ for 0.25 μ M and $k_{1st} = 6.0 \times 10^4 \text{ s}^{-1}$ for 5.0 μ M (Figure 3). Thus, it is considered that the small amount of the second-order part may be included in the decay in addition to the main unimolecular decay component. The existence of second-order component is also confirmed by the reciprocal plot in long time scale in Figure 3.

Next, we tried to determine the second-order rate constant of the slow-decay component $k_{2nd,slow}$. Using equation (5) with a fixed value of $k_{1st} = 5.11 \times 10^4 \text{ s}^{-1}$, each decay of 5.0 μ M P3OT solution is well fitted as is shown in Figure 3, although there were scattering of the data $k_{2nd,slow}/\epsilon_T = 5.0 \times 10^5 \text{ cm}^{-1}$ was obtained.

Then we tried to analyze the absorption time profile with a fast- and slow-decay component. The fast-decay component is considered to be independent from the slow-decay, since the fast-decay is far faster than the slow-decay. Equation (5) was applied for the slow-decay component, but it is difficult to determine whether the fast-decay obeys first- or second-order kinetics.

On assuming that the fast-decay is due to second-order kinetics, the time-dependent absorbance of both fast- and

slow-decay components is analyzed by equation (6), which is the sum of slow-decay component (first- and second-order kinetics) and fast-decay component (second-order kinetics)

$$\begin{aligned} \Delta\text{Abs} &= \Delta\text{Abs}_{\text{slow}} + \Delta\text{Abs}_{\text{fast}} \\ &= \frac{1}{\left(\frac{1}{\text{Abs}_{\text{slow},0}} + \frac{2k_{2nd,slow}}{\epsilon_T k_{1st}}\right) \exp(k_{1st}t) - \frac{2k_{2nd,slow}}{\epsilon_T k_{1st}}} \\ &\quad + \frac{1}{\frac{1}{\text{Abs}_{\text{fast},0}} + \frac{2k_{2nd,fast}}{\epsilon_T} t} \end{aligned} \quad (6)$$

where $\text{Abs}_{\text{fast},0}$ is the initial absorbance (at $t = 0$) and $k_{2nd,fast}$ is the kinetic rate constant of second-order fast-decay component. By applying equation (6) to dilute solution, each decay is fitted well as is shown in Figure 6, and the $2k_{2nd,fast}/\epsilon_T$ value was determined as $1.2 \times 10^8 \text{ cm}^{-1} \text{ s}^{-1}$.

In order to estimate the ϵ_T value of P3OT, a triplet energy transfer experiment from ${}^3\text{P3OT}^*$ to β -carotene was attempted by exciting P3OT in the presence of β -carotene. However, the absorption band of β -carotene is overlapped with that of P3OT at 355 nm, which retards the excitation of P3OT. Thus, the increase of the ${}^3\beta$ -carotene* rise at 550 nm produced from ${}^3\text{P3OT}^*$ was also small. By comparing the small rise of ${}^3\beta$ -carotene* with the accelerated decay of ${}^3\text{P3OT}^*$, the ϵ_T value of ${}^3\text{P3OT}^*$ was evaluated to be $2.83 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 800 nm, using the reference value of $\epsilon_T = 2.42 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ for T–T absorption of β -carotene at 550 nm³³.

On substituting $\epsilon_T = 2.83 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, $k_{2nd,fast}$ and $k_{2nd,slow}$ were calculated to be $1.36 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$ and $7.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, respectively. The $k_{2nd,slow}$ is similar to the diffusion controlled limit in THF ($1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) for the molecules with general diffusion coefficients such as 3T. The bimolecular event can be regarded as the inter-chain T–T annihilation. The diffusion controlled rate constant by

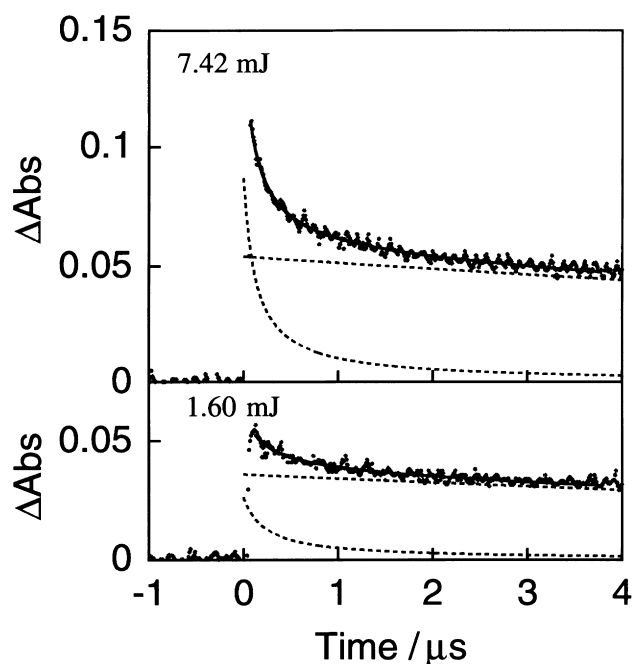


Figure 6 Absorption time profiles at 800 nm for 0.25 μ M in polymer unit of P3OT in THF obtained by various laser powers at 355 nm and the fitting curves by assuming equation (6)

Debye equation is usually applied to small molecules, such as 3T, with the assumption that the reaction radius is the same as the hydrodynamic radius of molecules. For macromolecule of P3OT in our study, the diffusion rate constant of polymer chain ($Pn = 406$) seems to be smaller at least two figures than that of 3T. The large value of $k_{2nd,slow}$ is probably due to the T–T annihilation via excessive fast excited triplet energy migration within the collision of the polymer chains. The energy migration effect in quenching of the excited singlet state has been carried out for side-chain type polymers^{34,35}. The enhancement of the quenching rate constant by the energy migration is discussed by introducing the excited singlet energy migration constant, in addition to the diffusion rate constant of the excited chromophore and the quencher. For the T–T annihilation process in P3OT, the excited energy migration within the collision spreads the reaction radius and thus the kinetic rate constant of inter-chain T–T annihilation may be enhanced.

Conversely, the intra-chain T–T annihilation process was indicated for side-chain type polymers in solution by laser flash photolysis¹⁸. The fast decay within 1 μ s was observed, which was assigned as intra-chain T–T annihilation at high triplet density and intra-chain self-quenching at low triplet density. For P3OT in this study, the possibility of self-quenching with neighboring sites in the ground state is very low because of the rather rigid main-chain. Furthermore, the rigid polymer spreads sufficiently in the highly soluble solvent THF, which renders interactions between non-neighboring highly unlikely.

However, if the fast-decay is assumed to be due to first-order kinetics, the time-dependent absorbance Δ Abs is analyzed by the sum of slow-decay component (first- and second-mixed order kinetics) and fast-decay component (first-order kinetics). Each decay is fitted well, but the rate constant of first-order fast-decay component $k_{1st,fast}$ increases from $2 \times 10^6 \text{ s}^{-1}$ to $4 \times 10^6 \text{ s}^{-1}$ with the density of triplet state moiety. The triplet state moiety density dependence of $k_{1st,fast}$ is difficult to interpret, and the assumption of the first-order kinetics for the fast-decay component may not be adequate. Then, the fast-decay is not obeying first-order kinetics but the bimolecular second-order kinetics, which may be intra-chain T–T annihilation; it seems reasonable to suppose that the T–T annihilation via energy migration is following the second-order kinetics.

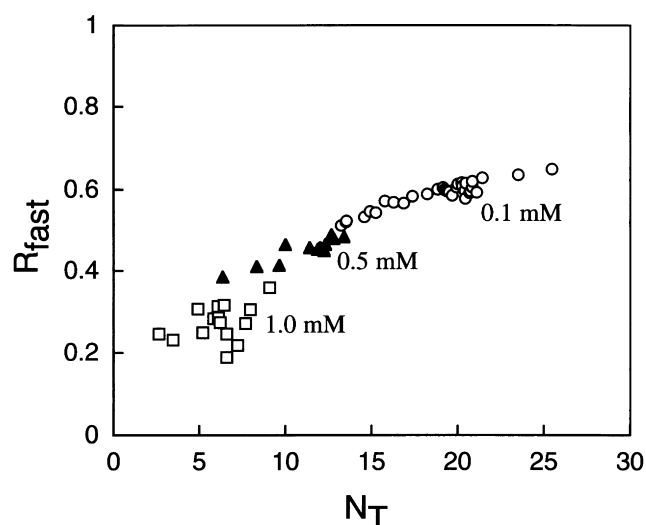


Figure 7 N_T dependence of R_{fast}

On the assumption of the intra-chain T–T annihilation occurring after triplet energy migration, it needs further consideration why all triplet state moieties do not deactivate with the far faster process of intra-chain T–T annihilation than the intrinsic deactivation process. The slow-decay component followed by the fast-decay indicates that all the triplet state moieties are not always deactivated by the fast intra-chain T–T annihilation after energy migration. The remaining triplet state moieties after extremely fast intra-chain T–T annihilation may be explained by considering any conformational irregularity and fluctuation of the polymer chain. These sites cut off the conjugation on the main-chain and some conjugated sequences may exist on a single polymer chain. The energy migration may be easily achieved and very fast within each conjugated sequence, but may be rather difficult and slow between neighboring conjugated sequences. Then, the fast-decay component of intra-chain T–T annihilation after energy migration occurs between triplet state moieties in the same conjugated sequence. For some conjugated sequences, a triplet state moiety may remain after intra-chain T–T annihilation and thus contribute to the slow-decay component. For the slow event of inter-chain T–T annihilation, the possibility of the energy migration between neighboring conjugated sequences may be larger than the fast intra-chain event. The energy migration along polymer chain contributes to the enlargement of the reaction radius in inter-chain T–T annihilation and the enhancement of the kinetic rate constant.

The ratio (R_{fast}) of the fast-decay component to the whole decay component is evaluated by dividing the absorbance decaying of fast-decay component within 1 μ s ($Abs_{fast,0}$) with the whole absorbance ($Abs_{fast,0} + Abs_{slow,0}$). The total number of the triplet state moiety in a chain (N_T) was calculated as follows

$$N_T = \frac{^3P3OT^*}{[polymer]} = \frac{(Abs_{fast,0} + Abs_{slow,0})/\epsilon_T}{[monomer]/Pn} \quad (7)$$

where, polymerization degree (Pn) is 406 for our P3OT. The R_{fast} values are plotted against N_T as shown in Figure 7. The ratio of fast-decay component, which is assigned to intra-chain T–T annihilation, indicates the same dependence on the numbers of triplet state moiety in a polymer chain, N_T , over different polymer concentrations. The intra-chain T–T annihilation is the internal polymer process and is independent of the external concentration of the polymer. The second-order kinetic rate constant of fast-decay component is three orders of magnitude larger than that of the slow-decay component. The far faster intra-chain process and the slower inter-chain process are characteristic phenomena of conjugated polymers.

From the decay curves observed at 0.25 μ M polymer concentration (Figure 6), N_T and R_f are evaluated to be ca. 20 and 0.6, respectively, for laser power = 7.42 mJ. The total number of the triplet state moieties in a chain decrease from ca. 20 to ca. 8 after the intra-chain T–T annihilation process within 1 μ s. At low laser power (1.60 mJ), about 9 excited states are formed in 406 thiophene moieties and about 4 of them disappear rapidly with the intra-chain events within 1 μ s. At high laser power (6.51 mJ) of high polymer concentration (5 μ M), about 5 triplet states are formed and no fast-decay component is observed.

These findings suggest that about 5 to 8 excited states can be persistent in each 406-mer polymer chain after intra-chain T–T annihilation. These 5 excited states remaining after fast decay contribute to the slow-decay component of

intrinsic deactivation process and inter-chain T–T annihilation. The fast and highly efficient deactivation processes of delocalized excited triplet states along the polymer chain, which is not observed in side-chain type polymers, are the characteristic phenomena of π -conjugated polymers.

CONCLUSION

Dynamics of the excited triplet state of π -conjugated poly(3-n-octylthiophene) in solution exhibits quite different behavior from that of the thiophene oligomer. The extremely fast-decay component of T–T absorption band was observed in addition to the slow one. The fast-decay component was assigned to intra-chain T–T annihilation and slow one to intrinsic lifetime and inter-chain T–T annihilation. The existence of two deactivations of quite fast intra-chain process and slow inter-chain process is characteristic of π -conjugated polymers.

REFERENCES

- Guillet, J. E., *Polymer Photophysics and Photochemistry*. Cambridge University Press, Cambridge, 1985, Chapter 9.
- Guillet, J.E., Hoyle, C.E. and MacCallum, J.R., *Chem. Phys. Lett.*, 1978, **54**, 337.
- MacCallum, J.R., Hoyle, C.E. and Guillet, J.E., *Macromolecules*, 1980, **13**, 1647.
- North, A.M. and Ross, D.A., *J. Polym. Sci., Symp.*, 1976, **55**, 259.
- North, A.M. and Treadaway, M.F., *Eur. Polym. J.*, 1973, **9**, 609.
- North, A.M., Ross, D.A. and Treadaway, M.F., *Eur. Polym. J.*, 1974, **10**, 411.
- Samuel, I.D.W., Crystall, B., Rumbles, G., Burn, P.L., Holmes, A.B. and Friend, R.H., *Chem. Phys. Lett.*, 1993, **213**, 472.
- Lemmer, U., Mahrt, R.F., Wada, Y., Greiner, A., Bässler, H. and Göbel, E.O., *Chem. Phys. Lett.*, 1993, **209**, 243.
- Samuel, I.D.W., Crystall, B., Rumbles, G., Burn, P.L., Holmes, A.B. and Friend, R.H., *Synth. Met.*, 1993, **54**, 281.
- Kobayashi, T., *Synth. Met.*, 1992, **49-50**, 565.
- Kobayashi, T., *Synth. Met.*, 1993, **54**, 75.
- Kobayashi, T. and Yoshizawa, M., *Synth. Met.*, 1991, **41-43**, 3129.
- Kersting, R., Lemmer, U., Mahrt, R.F., Leo, K., Kurz, H., Bässler, H. and Göbel, E.O., *Phys. Rev. Lett.*, 1993, **70**, 3820.
- Kaeriyama, H., Towa, T., Hagquist, G.W., Ito, S. and Yamamoto, M., *Macromolecules*, 1993, **26**, 265.
- David, C., Baeyens-Volant, D., Macedo de abreu, P. and Geuskens, G., *Eur. Polym. J.*, 1977, **13**, 841.
- Kiwi, J. and Schnabel, W., *Macromolecules*, 1975, **8**, 430.
- Hayashi, K., Irie, M., Kiwi, J. and Schnabel, W., *Polym. J.*, 1977, **9**, 41.
- Schnabel, W., *Makromol. Chem.*, 1979, **180**, 1487.
- Tsuchida, A., Yamamoto, M., Liebe, W.R., Burkhardt, R.D. and Tsubakiyama, K., *Macromolecules*, 1996, **29**, 1589.
- Sugimoto, R., Takeda, S. and Gu, H.B., *Chem. Express*, 1986, **1**, 635.
- Yoshino, K., Nakajima, S. and Gu, H.B., *Jpn. J. Appl. Phys.* 2, 1987, **26**, L2046.
- Sato, M. and Horii, H., *Macromolecules*, 1991, **24**, 1196.
- McCullough, R.D., Lowe, R.D., Jayaraman, M. and Anderson, D.L., *J. Org. Chem.*, 1991, **58**, 904.
- Botta, C., Luzzati, S., Tubino, R. and Borghesi, A., *Phys. Rev.*, 1992, **B 46**, 13008.
- Heffner, G.W. and Pearson, D.S., *Macromolecules*, 1991, **24**, 6295.
- Watanabe, A. and Ito, O., *J. Phys. Chem.*, 1994, **98**, 7736.
- Kodaira, T., Watanabe, A., Ito, O., Watanabe, M., Saito, H. and Koishi, M., *J. Phys. Chem.*, 1996, **100**, 15309.
- Watanabe, A., Kodaira, T. and Ito, O., *Chem. Phys. Lett.*, 1997, **273**, 227.
- Wintgens, W., Valat, P. and Garnier, F., *J. Phys. Chem.*, 1994, **98**, 228.
- Reyftmann, J.P., Kagan, J., Santus, R. and Morliere, P., *Photophys. Photobiol. V*, 1985, **1**, 1.
- Becker, R.S., De Melo, J.S., Maçanita, A.L. and Elosei, F., *Pure Appl. Chem.*, 1995, **67**, 9.
- Debye, P., *Trans. Electrochem. Soc.*, 1942, **82**, 265.
- Bensasson, R., Dawe, E.A., Long, D.A. and Land, E.J., *J. Chem. Soc., Faraday Trans.*, 1977, **73**, 319.
- Hargreaves, J.S. and Webber, S.E., *Macromolecules*, 1984, **17**, 235.
- Webber, S.E. and Avots-Avotins, P.E., *Macromolecules*, 1981, **14**, 105.